NASA-CR-192114

IN-91-CR
143811
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THEORETICAL STUDIES OF IMPORTANT PROCESSES IN PLANETARY AND COMET ATMOSPHERES

Semi-Annual Status Report

November 1, 1990 - April 30, 1991

NASA Grant NAGW 1404

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(NASA-CR-192114) THEORETICAL STUDIES OF IMPORTANT PROCESSES IN PLANETARY AND COMET ATMOSPHERES Semiannual Status Report, 1 Nov. 1990 - 30 Apr. 1991 (Inst. for Scientific Research) 11 p

N93-19959

Unclas

G3/91 0143811

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This is the fifth semi-annual progress report describing research on dissociative recombination reactions in planetary and comet atmospheres.

The Appendix has two papers that describe NASA supported research. Both papers have been recently accepted for publication. The first paper, "The Generation of $O(^1S)$ from the Dissociative Recombination of O_2^+," describes in detail the Multichannel Quantum Defect (MQDT) theory used for the calculation of dissociative recombination (DR) cross sections and rates. The application to the generation of the upper state of the atomic oxygen green line emission is of great importance to the modelling of planetary atmospheres. The paper describes the role of the Rydberg resonances in determining the shape of the cross sections. We show that both a vibronic mechanism and a second order electronic mechanism are involved in populating the Rydberg states. This is the first paper to explain the origin of the shape of the resonance cross sections using Fano profile indices for both the vibronic and electronic couplings. The second paper in the Appendix, "Dissociative Recombination of the Ground State of N_2^+," applies the methods described in the first paper to N_2^+. We find remarkable agreement with the prior microwave afterglow experiments for both the total recombination rate and for its electron temperature dependence. However, the results disagree with recent merged beams results which gave cross sections that are a factor of five below both the microwave afterglow experiments and the current results. DR of N_2^+ is an important mechanism for generating energetic N atoms which can escape the atmosphere of Mars. A prior plasma flow tube experiment found that most of the recombination generated N atoms with insufficient

kinetic energy to escape Mars. However, the theoretical results obtained in this laboratory show that the main DR channel, $C'^3\Pi_u$, leads primarily to N atoms with sufficient energy to escape. We believe that the accuracy of our results indicates that the experiments are observing vibrationally excited and not ground state N_2^+. The theoretical results show that DR of N_2^+ is a very important mechanism in generating hot N atoms which can escape the Martian atmosphere. Also, this mechanism will strongly influence the N^{15}/N^{14} isotope ratio.

Currently we are also continuing additional work on the DR of O_2^+ which is aimed at calculating both the total DR rate as a function of ion vibrational level and the rate for production of $O(^1D)$. The Rydberg resonances will be included as described in the first paper in the Appendix. From prior work in this laboratory we know that only six states have electron capture widths that are large enough to be important in DR of the lowest 10 vibrational levels of O_2^+. Theses states are $1^3\Pi_u$, $1^1\Pi_u$, $c^1\Sigma_u^-$, $1^1\Delta_u$, $^1\Sigma_u^+$, and $B^3\Sigma_u^-$. The first three states yield only ground state atoms upon dissociation. Potential curves for the first two states are currently being calculated. The calculation of the potential curve of the $c^1\Sigma_u^-$ state has been completed and is shown in Figure 1. The potential curve crosses the ion curve near the inner turning point of the v=4 level. The curve was obtained in a configuration interaction (CI) calculation having 305,920 terms and was determined using a CRAY YMP computer. A total of 44 points were determined on the potential curve between 1.8 and 8.0 Bohr. The shape of the curve agrees well with experiment. Of course there is no experimentally derived result for the high repulsive wall near the ion crossing and the current calculations provide this information. The calculated (experimental)[1] results for the spectroscopic constants are 767(794)cm^{-1} for ω_e,

12.7(12.7)cm^{-1} for $\omega_e x_e$, 2.8972(2.8674)a_o for R_e, 0.997(1.115)eV for the dissociation energy and 3.98(4.10)eV for T_e.

The method used for the width calculations has been described previously[2,3,4,5] and in the original proposal. The widths are obtained by including a large Rydberg basis set at the molecular midpoint and calculating a series of high Rydberg orbitals using the IVO method.[6] The widths determined from the highest Rydberg orbitals are then used to calculate the free electron capture width. The width is the hamiltonian matrix element between the dissociative valence configuration interaction (CI) wave function for states discussed in the prior paragraph and a CI wave function for a high Rydberg state. Since the ground state of O_2^+ has $^2\Pi_g$ symmetry, a large basis of π_u Rydberg Gaussian basis functions was placed at the molecular midpoint in order to form $^1\Sigma_u^-$ Rydberg states. The valence space is described with a double zeta plus polarization Gaussian basis set. The Rydberg basis set has 18 primitives with exponents, α, obtained from the expression[7]

$$\alpha = (1/2m)^2 \, (1/(0.382362m + .251333))^2,$$

where m runs from 1.0 to 9.5 with a 0.5 increment. We found that this approach provides for excellent descriptions of high Rydberg states.

In Table 1 below results are shown for calculations on the states of $^1\Sigma_u^-$ symmetry. The Rydberg levels are labelled with the effective principal quantum number, n*, where $n^*=n-\mu$ and n and μ are the principal quantum number and quantum defect, respectively. Since the Rydberg states calculated here are diabatic states having mostly the π_u character, μ should be nearly constant with n* for high n if the Rydberg basis set description is accurate. Note that μ=0.745 and 0.746 for n*(n)=9.255(10) and 8.254(9) respectively. The quantum defects are not expected to be constant for the

lowest levels because the interaction between the Rydberg orbital and the valence orbitals is still significant. The levels with n*=7.253, 8.254, and 9.255 levels have nearly constant μ. The deviation at n*=10.27 is due to the inadequacy of the basis set. The widths are also nearly constant except for the highest level. The free electron threshold capture widths can therefore be obtained from the n*=9.255 or 8.254 level.

	Γ(eV)
n*	$c\ ^1\Sigma_u^-$
10.27	0.2036
9.255	0.2064
8.254	0.2061
7.253	0.2059
6.2523	0.2054
5.2500	0.2047
4.2461	0.2037
3.2377	0.2020
2.2135	0.1992

Table 1. Calculated effective principal quantum numbers, n*, and electron capture widths for the $c^1\Sigma_u^-$ state of O_2.

Using the above calculated width we have calculated the DR cross sections and rates along the $^1\Sigma_u^-$ dissociative channel which leads to $O(^3P) + O(^3P)$. Fig.2 shows the calculated DR cross section for the v=0 ion vibrational level for electron energies up to 1eV. The cross section that has no structure (dashed line) is the "direct" DR cross section in which the resonance states are excluded. The solid line shows the full cross section including the resonance states. In the calculations we include levels up to n=25. The first resonance shown in Fig.2 at 0.03eV corresponds to the n=9,v=1 Rydberg level followed by the n=10,v=1 level at 0.07eV. Both these resonances have a similar shape, however n=10 is more contracted. The resonances get narrower as n increases. Note that at very low electron energies the cross section which includes the resonances (the full cross section) is below the cross section without the resonances. This difference is due to the n=3,v=14 and n=4, v=6 resonances which are below the v=0 level. While this state is discrete with respect to the v=0 electron-ion continuum it has a wing which extends above threshold.

Fig. 3 has the rate derived from the cross sections shown in Fig. 2. The full rate is shown as a solid line while the rate without the resonances is shown as a dashed line. The full rate at 300K is only 4.6×10^{-11} cm^3/sec. The rate is very small because the dissociative route does not cross the ion between the turning points of v=0. We have done calculations on excited vibrational levels. As expected from the crossing shown in Fig.1 the rate increases with increasing ion vibrational level. For v=1, the rate near 300K is 3.2×10^{-10} cm^3/sec and the rate increases to 2.9×10^{-9} cm^3/sec for v=4.

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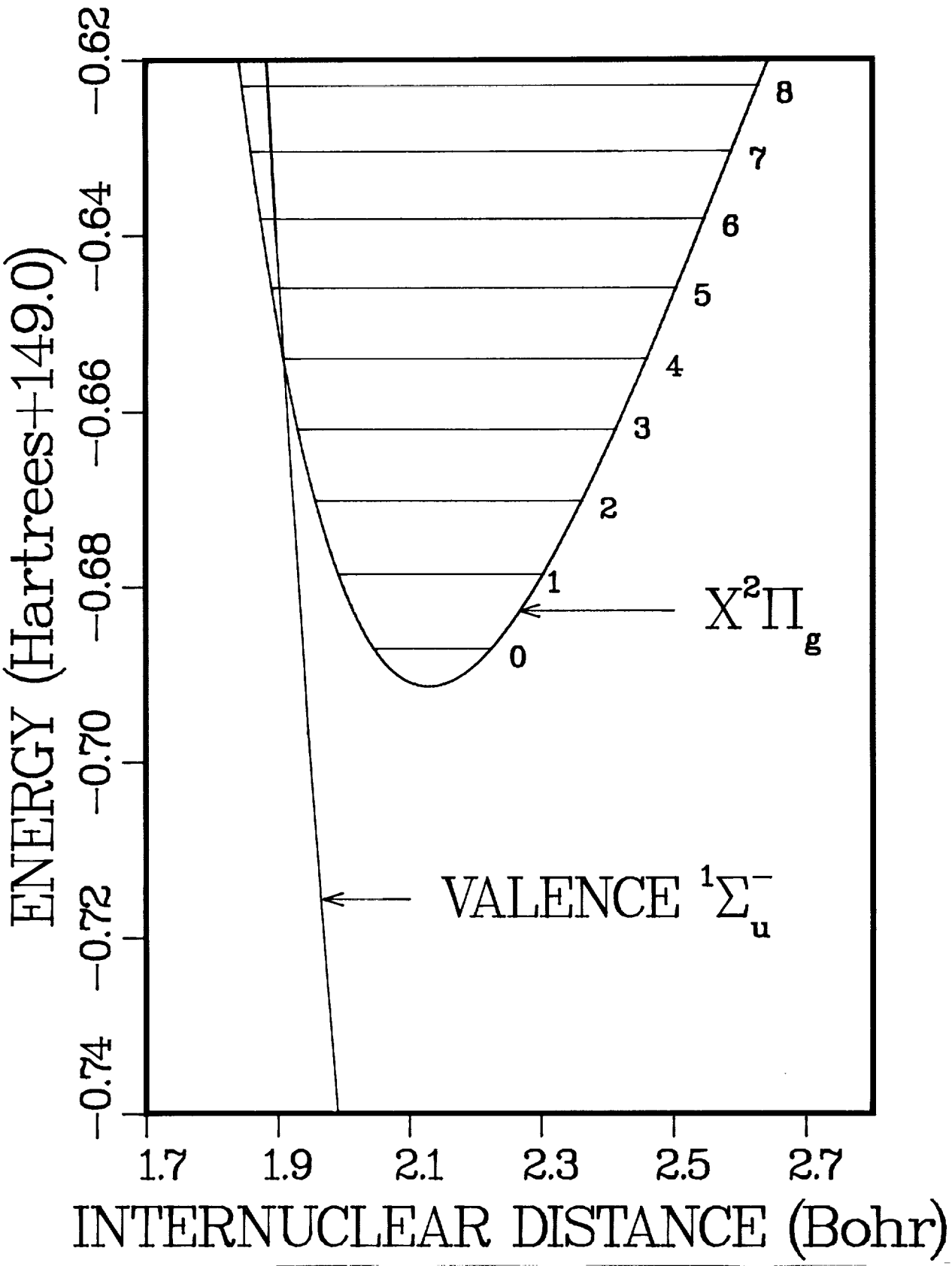

Figure 1. The dissociative state and ion potential.

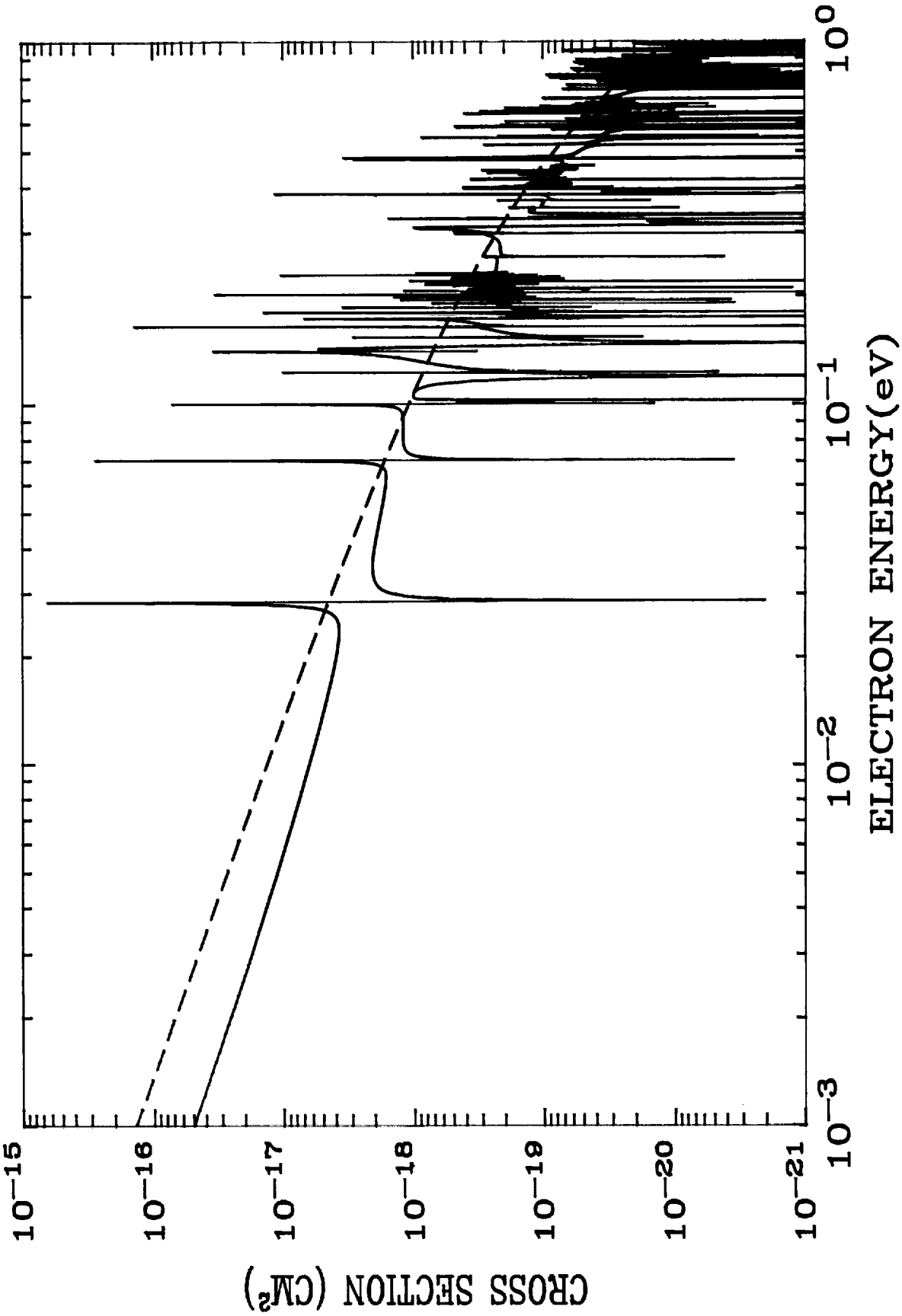

Figure 2. The direct (dashed) and full (solid line) DR cross section from the v=0 ion level.

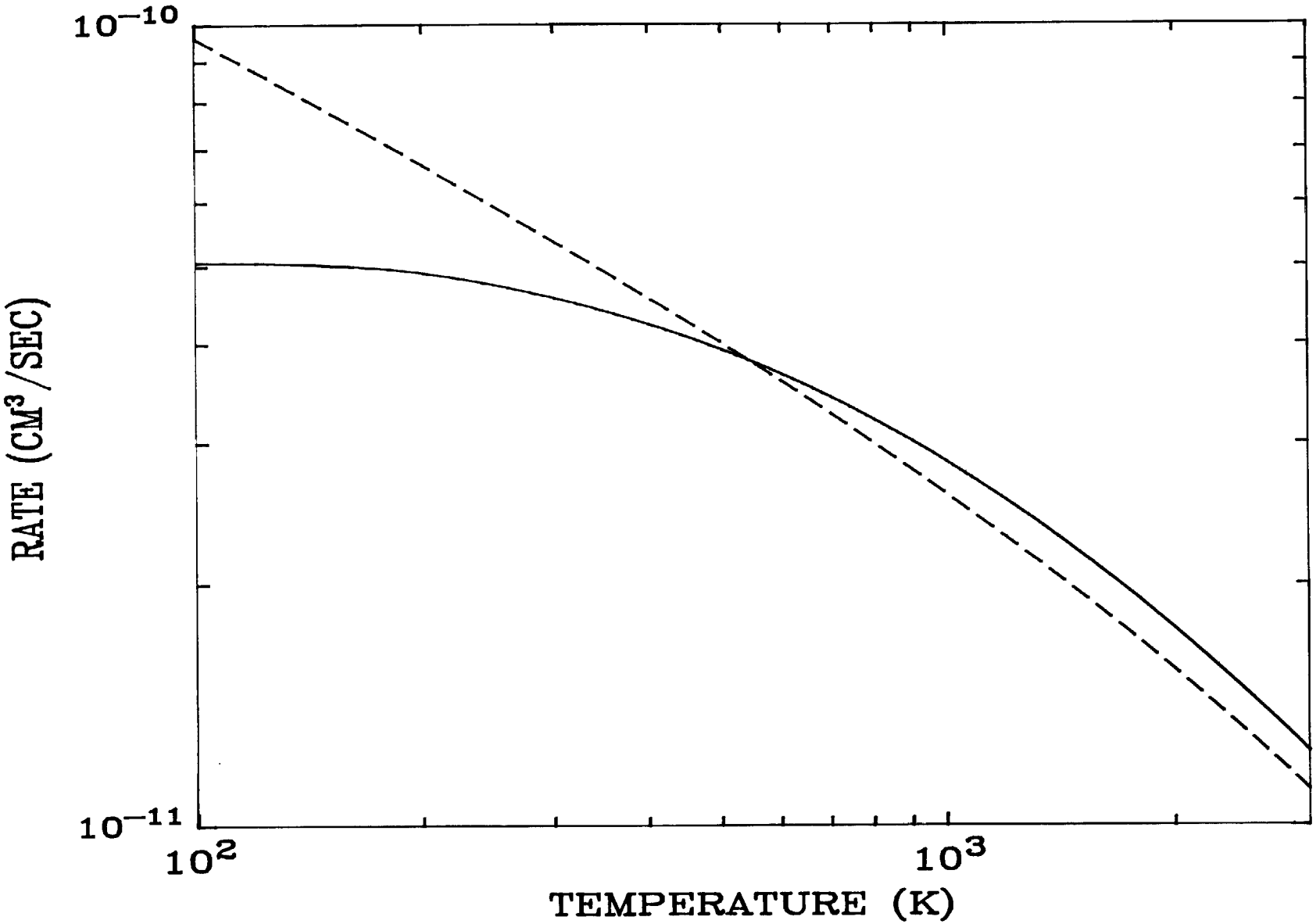

Figure 3. The direct (dashed) and full (solid line) rates for DR from the v=0 ion level.

Appendix

1. S. L. Guberman and A. Giusti-Suzor, The Generation of $O(^1S)$ from the Dissociative Recombination of O_2^+, Journal of Chemical Physics, in press (1991).

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